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Resolution of DPASV Overlapping Peaks of Indium and Cadmium in Trace Analysis of High Purity Gallium Arsenide

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Computer-aided resolution of overlapping differential pulse anodic stripping voltammetry peaks of In and Cd is proposed for trace determination in high purity gallium arsenide. It is based on the fact that the signal of In appears only if the analyzed solution contains chlorides, while Cd produces signal even in the chloride-free medium. The signal of Cd obtained in the GaAs sample solution in HNO₃ is corrected to the chloride-containing medium before subtraction from the sum of unresolved peaks of In and Cd registered in the GaAs sample solution in the HNO₃—HCl mixture. The procedure was tested on ultrapure GaAs samples spiked with Cd and In. It was then applied to trace analysis of Cd and In of some industrial high purity GaAs samples.

Anodic stripping voltammetry (especially in the differential pulse mode — DPASV) on a Hg stationary electrode is commonly applied for determining impurities in high purity substances used in semiconductor components production [1]. Common metallic trace impurities of GaAs excepting In and Cd can be easily determined by this method directly in the acidic sample solution without any further adjustment since their stripping peaks are sufficiently separated. The In and Cd peak potential difference (40 mV), however, is still sufficient for their simultaneous determination by DPASV at the concentration level above 0.1 μmol dm⁻³ and with the concentration ratio close to unity. At lower concentrations and the ratio significantly differing from unity it is necessary to separate their overlapping signals.

EXPERIMENTAL

All used chemicals were of anal. grade purity. With the exception of the isothermally distilled HNO₃ they were used without any further purification. Standard solution 10⁻³ mol dm⁻³ of In³⁺ was prepared by dis-

solution of the corresponding amount of metal in 10 cm³ of the concentrated acids mixture HCl—HNO₃ (φ_r = 3 : 1, heated if necessary) and dilution to 100 cm³ with triply distilled water. Standard solution of Cd²⁺ was prepared directly from its chloride salt.

A PA 4 polarographic analyzer (Laboratorní přístroje, Prague) was used for electrochemical analysis in DPASV adjustment. Set parameters were as follows: cathodic deposition potential – 0.70 V vs. SCE, time 240 s; anodic stripping scan rate 10 mV s⁻¹, pulse height 12.5 mV, pulse frequency 5 Hz. Computer Compucorp 610 (Compucorp, Los Angeles, USA) equipped with A/D and D/A convertors (Burr-Brown, Tucson, USA (maximum sampling frequency 5 kHz)) on line with the electrochemical instrument was used for taking experimental curves (1000 points) and following processing of experimental data. Hanging mercury drop working electrode (HMDE) had the active surface area 1.64 mm².

Sample Solution Preparation

0.5 g of powdered solid GaAs was dissolved in 5 cm³ of the mixture of concentrated acids HCl—

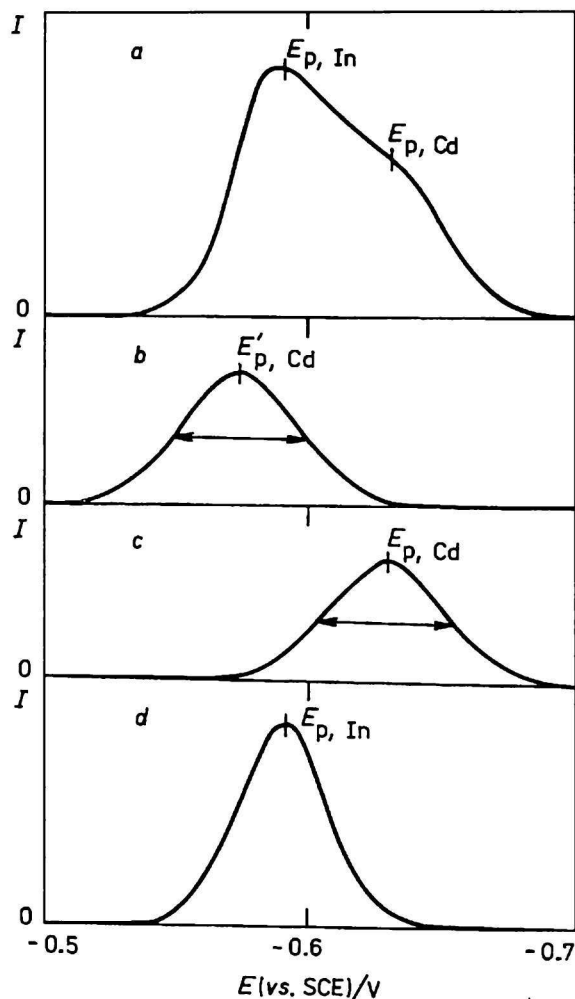


Fig. 1. Computer-aided procedure of the resolution of DPASV overlapping peaks in the trace analysis of In and Cd in GaAs (voltammograms after subtraction of the background current). Conditions of determination are specified in Experimental. a) Voltammogram of GaAs solution in the mixture of acids HCl–HNO₃ ($\varphi_r = 3 : 1$) (overlapping peaks of In and Cd; $E_{p,Cd} - E_{p,In} \approx 40$ mV); b) voltammogram of GaAs solution in HNO₃; c) voltammogram *b* after computer correction of the Cd peak potential and peak height for the change of media; d) curve of the resolved peak of In as a result of computer subtraction of curves *a* and *c*.

HNO₃ ($\varphi_r = 3 : 1$) or 5 cm³ of concentrated HNO₃. Solution was heated if necessary and its volume was adjusted to 50 cm³ with triply distilled water. The same acid volumes and procedure were used for blank solutions preparation which served for background corrections.

RESULTS AND DISCUSSION

The resolution of DPASV overlapping peaks of In and Cd is based on the fact that the composition of the supporting electrolyte has an important influence on the determination of In(III) by both polarography

and anodic stripping voltammetry. Moorhead and MacNevin [2] found that in noncomplexing media (e.g. such as nitrate) In(III) did not produce a polarographic reduction wave. Only in halide or thiocyanate media well-formed polarographic waves were found [2–4]. A strongly complexing medium is also necessary for the determination of In by anodic stripping voltammetry [5–7]. To resolve the overlapping peaks of In and Cd it is proposed to subtract the signal of Cd from the sum of analyzed peaks by a computer procedure. The subtracted signal of Cd can be obtained by DPASV analysis in solution of GaAs in HNO₃ without HCl. The DPASV peak of Cd, however, can generally have different parameters (peak height, peak potential, and peak width) in different media. As follows from Fig. 1 the signal is shifted to the more positive potential in the absence of chloride. That is why it is necessary to correct the Cd peak obtained from experiment in HNO₃ for the change in Cl[−] concentration. These correction factors for a typical chloride concentration of the analyzed solution 1 mol dm^{−3} were found by using ultrapure GaAs spiked with Cd. Two solutions prepared from equal amounts of the ultrapure GaAs (containing less than 1/100 of spiked amount Cd) were spiked by Cd in the amount corresponding to 1×10^{-7} mol dm^{−3} Cd²⁺ in the analyzed solution. In the first case only HNO₃ and in the second both HCl and HNO₃ ($\varphi_r = 3 : 1$) were used for dissolution of GaAs. The same amounts of acids were used for preparation of the blank solution for background correction. DPASV signals of Cd²⁺ were registered in both solutions. It was found that in a chloride-containing medium the Cd²⁺ peak potential is shifted by $E_{p,Cd} - E'_{p,Cd} = -58$ mV, peak height decreased by 4.7 % and the peak width remained practically unchanged (Fig. 1, curves *b*, *c*). The corrections were found to be independent of the chloride concentration in the range 0.4 mol dm^{−3} to 1.2 mol dm^{−3}. In the GaAs sample solution prepared by the procedure described in Experimental with the mixture of concentrated HCl and HNO₃ the concentration of Cl[−] is ca. 1 mol dm^{−3}. Stripping voltammogram taken in the solution of GaAs in HNO₃ with a single Cd peak was registered (Fig. 1, curve *b*), and its peak height was corrected by multiplication by 0.953. The peak was then shifted by -58 mV (Fig. 1, curve *c*) and afterwards subtracted from the unresolved experimental curve taken in the solution of GaAs in the HCl–HNO₃ mixture (Fig. 1, curve *a*). The DPASV voltammogram after subtraction (Fig. 1, curve *d*) exhibits only one peak of In.

The procedure was tested using five samples of ultrapure GaAs spiked with standards of Cd²⁺ and In³⁺, with five repetitions of determination for each sample (Table 1). For the evaluation the method of multiple standard addition was used. Standard additions proved the linear proportionality of DPASV

Table 1. Statistical Evaluation of the In and Cd Determination in Spiked GaAs Samples by Resolution of Overlapping DPASV Peaks. Found Values Are Average of Five Parallel Determinations

Sample	Content w/ppb ^a				Limits of confidence for 95 % probability/%	
	Given		Found (mean)			
	In	Cd	In	Cd	In	Cd
1	10	70	12	75	120 ± 33	107 ± 18
2	20	60	18	65	90 ± 25	108 ± 15
3	40	40	42	38	105 ± 15	95 ± 18
4	60	20	64	19	107 ± 12	95 ± 30
5	70	10	76	8	109 ± 15	80 ± 35

a) In and Cd added to the solution of ultrapure GaAs.

signal on the contents of Cd²⁺ and In³⁺. Results of the determination in spiked solutions summarized in Table 1 show that the arithmetic mean of parallel determinations does not differ statistically from the given values. The reliability interval is well acceptable taking into account the low concentration level of determined species.

The method was applied for the determination of trace amounts of In and Cd in some high purity GaAs samples. Results of the analysis are given in Table 2. Method of standard addition was used for the determination of In and Cd.

Table 2. Results of In and Cd Determinations in Some Industrial Samples of High Purity GaAs

Sample	Content in GaAs w/ppb	
	In	Cd
1	11 ± 3	5 ± 3
2	22 ± 3	10 ± 5
3	13 ± 3	12 ± 3
4	19 ± 3	12 ± 5
5	12 ± 3	20 ± 5
6	10 ± 3	20 ± 5
7	13400 ± 200	23 ± 10
8	10 ± 3	11 ± 3

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